Dedicated to the memory of David T Thompson

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CO oxidation: Deactivation of Au/TiO_2 catalysts during storage

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Abstract

In a study of the phenomenon of catalyst deactivation during storage, Au/TiO_2 catalyst was stored under various conditions, viz. vacuum, nitrogen, air, refrigeration, dark, and light, and tested for CO oxidation activity at regular intervals. The data shows that the catalyst deactivates under all the storage conditions over 12 months and that storage in vacuum significantly enhances the rate and extent of deactivation. Storage in light accelerates the deactivation. The catalyst appears to deactivate through a combination of Au(III) reduction, Au nanoparticle agglomeration, loss of surface hydroxyl groups, loss of surface moisture, and accumulation of surface carbonates and formates. The rate and extent of catalyst deactivation can be limited by storing the catalyst in the dark at sub ambient temperature (refrigerator) and under inert atmosphere.

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1 Introduction

A lot of attention has been given to gold as a catalyst since the discovery that it can oxidize carbon monoxide at extremely low temperatures [1]. One of the drawbacks of highly active gold catalysts, which are delaying technology development, is the fact that they deactivate both in storage and on-line [2].

Gold catalysts can be deactivated on-line by particle size agglomeration [3], carbonate formation and build up [4], as well as removal of hydroxyl groups from active sites [5]. Based on the previous infrared study from our group, we have agreed with some of the literature data that suggest the negative effect of carbonate species on the surface of the working catalyst [6]. Catalyst deactivation by carbonate formation was reported to be a reversible phenomenon, due to the fact that it is accompanied by the removal of moisture from the catalyst. The re-introduction of moisture to the surface of the catalyst can therefore regenerate the catalyst provided the deactivation was not caused in part by particle size agglomeration [1, 2 and 5]. Deactivation of gold catalysts was also observed during storage and it is necessary to determine if the factors that deactivate the catalyst on-line are the same as those that deactivate the catalyst during storage.

To avoid catalyst deactivation during storage, appropriate storage conditions need to be established where catalysts will retain their activity over a long period of time. Haruta and co-workers [7] observed an increase in the particle size of gold when the dried catalyst is stored in ambient air and recommended storage in the freezer at temperatures below 0°C. On the other hand, Zanella *et al*. [3, 8] reported that to avoid deactivation by sintering, the catalyst should be stored after preparation and drying under vacuum in a desiccator containing

dried silica gel, which should be maintained in a dark environment. In this paper, we present a systematic study on the effect of refrigeration, vacuum, light, dark and inert gas storage on a fresh Au/TiO_2 catalyst dried at 120°C.

2 Experimental procedures

2.1 Catalyst preparation

The catalyst was prepared by the deposition precipitation method. Under constant stirring, 50 g_{Au}/l $HAuCl_4$ was added to the necessary amount of deionised water and heated to 70°C. The pH of the solution was altered to pH=7.5 over a period of 10 minutes using 0.5 M Na_2CO_3 solution. The support (Degussa, 7711 P25, TiO_2) was added into the gold bearing solution and aged with constant stirring for 1 hour at 70°C while the pH was kept constant using 0.5 M Na_2CO_3 and 2 M HNO_3. After the prescribed ageing period the material was filtered and thoroughly washed with deionised water. The catalyst was then dried at 120°C for a period of 16.5 hours in a fan assisted oven.

2.2 Catalyst characterization

Infrared (IR) absorptions were measured with a Fourier Transform (FT)-Raman 5700 Nicolet spectrometer from Thermo Electron Corporation equipped with a Collector DRIFTS cell and a high pressure and temperature chamber. A small amount of the catalyst was ground into a fine powder and loaded into a DRIFTS cell without any dilution with KBr. 64 scans were collected per analysis at resolution of 8.

For X-ray photoelectron spectroscopy (XPS) studies, a Quantum 2000 Scanning ESCA Microprobe was used. The catalyst was ground and pressed into the sample holder to remove all the air trapped in between the catalyst powder particles. The area of analysis for each catalyst was 500 x 500 µm. A monochromized aluminium K_α source was used as an X-ray source to produce a beam of 100 µm diameter and 20 W power. The base vacuum was 8 x 10^{-9} torr. A charge neutralizer to produce a low flood of electrons and argon ions was used. The carbon 1s peak at 285.0 eV was used for the peak position correction. The pass energy of 117 eV was used for the wide scan, while charge energy of 27 eV was used for a narrow scan. XPS is primarily a surface technique, as the escape depth of the photo-electrons ranges from 2 to 5 nm. The detection limit of XPS is approximately 0.1 at.% Au catalysts tend to reduce in-situ during the XPS analysis due to surface charging effects caused by XPS irradiation [9, 10, 11]. However, to confirm the extent of gold reduction by storage, Pulse Temperature Programmed Reduction studies were performed on the stored and fresh catalysts before XPS analysis.

Pulse Temperature Programmed Reduction (P-TPR) was performed using the Micrometrics AutoChem II – 2920 chemisorption analyser. 0.060g of the catalyst was first heated gently to 110°C under argon. 0.3 ml pulses of the reducing gas mixture (10.5% H_2/Ar) were passed over the material. A portion of hydrogen in each pulse will be consumed until all the Au(III) initially present in the catalyst has been reduced. The total amount of Au(III) in the catalyst can be calculated from the total amount of hydrogen consumed.

A JEM-2100F Transmission Electron Microscope (TEM) was used to establish the dispersion and the particle size of the Au on the surface of the support. The catalyst was ground and mixed with ethanol. A droplet of the ethanol solution was placed on the carbon-coated copper grids. The sample was left at room temperature for a few minutes to dry before being loaded into the microscope.

2.3 CO oxidation

The activity of CO oxidation was tested on a flow reactor connected to a Signal IR detector by exposing 25 mg of the catalyst placed in a U-tube to a mixture of 1% CO and 20% O_2 balanced by nitrogen at 500 ml/min.

2.4 Storage

One batch of Au/TiO_2 catalyst was divided into a number of samples which were stored at ambient temperature in the light and in the dark, as well as in the dark at ~4°C (refrigerator). In each of these environments, three samples were stored under nitrogen, air and vacuum as shown in Table 1. For the storage in the dark, the vials containing the catalyst

Table 1

Light (ambient temp)	Dark (ambient temp)	Dark (~4°C)
nitrogen	nitrogen	nitrogen
air	air	air
vacuum	vacuum	vacuum

The environments in which Au/TiO_2 catalysts were stored

were wrapped in a foil and stored in a photographic dark room. The catalysts stored in the light were placed on a laboratory windowsill. The activity of these catalysts was monitored regularly. The catalysts were characterized by several techniques after 12 months' storage.

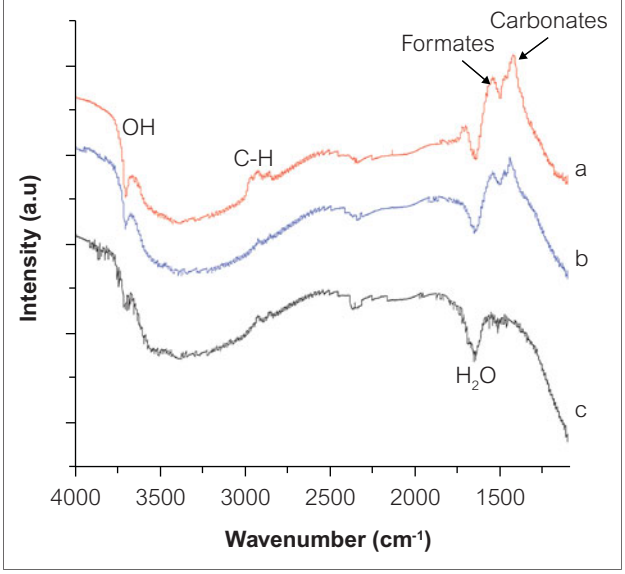
3 Results and discussion

3.1 Catalysts characterization

3.1.1 Storage in the light (ambient temperature)

Changes on the surface structure of the catalysts after storage in various environments were monitored by infrared spectroscopy. From each spectrum of a stored catalyst, a spectrum of a fresh catalyst was subtracted to give the difference between the two. The resultant spectrum shows both negative and positive peaks, where the negative peaks indicate the loss of the surface species [12] and the positive peak indicates the formation or the presence of a new species. Water equilibrates with the catalysts surface very quickly; so catalysts stored under a particular storage environment were all analysed within a short time period of each other to avoid differences in the amount of atmospheric moisture that would adsorb on the surface. During analysis each catalyst was only exposed to the ambient relative humidity of the laboratory for ~6 minutes. Since all catalysts were treated in the same way it seems reasonable to assume that changes observed by IR are due to the effect of storage.

Figure 1

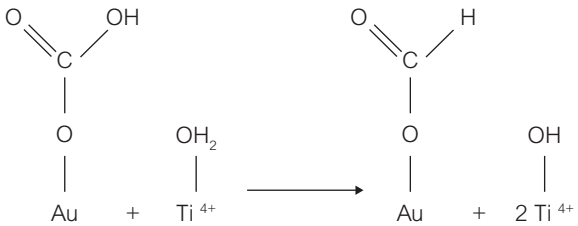


Infrared spectra of Au/TiO_2 catalyst stored in the light under various environments; (a) Vacuum; (b) Air; (c) Nitrogen

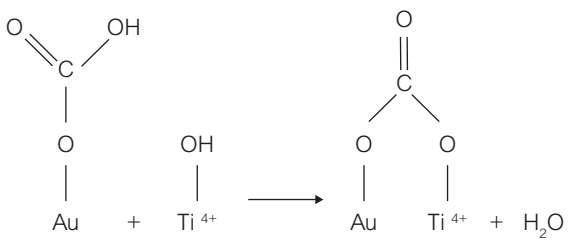
The infrared spectra in Figure 1 show the results after storage in the light. There is loss of moisture and hydroxyl groups from the surface of the catalysts. This is evidenced by the negative peaks between 4000 and 3000 cm^{-1}. These are accompanied by negative peak around 1620 cm^{-1} which corresponds to the bending mode of the water molecule confirming the loss of moisture [12]. Figure 1a reveals that if the catalyst is stored under vacuum, the loss of moisture is accompanied by the formation of formate and carbonate species on the surface, as shown by new peaks between 1620 cm^{-1} and 1400 cm^{-1}. Formation of formate species is further confirmed by the appearance of C-H stretches at 2855 and 2930 cm^{-1}.

A fresh catalyst has relatively high amounts of moisture and hydroxyl groups on its surface. Bicarbonate species are formed by the reaction between atmospheric CO_2 and surface hydroxyls during catalyst preparation [6]. During vacuum storage, moisture and bicarbonates decompose to form formate species [6] and more OH groups as shown in reaction scheme 1.

Scheme 1

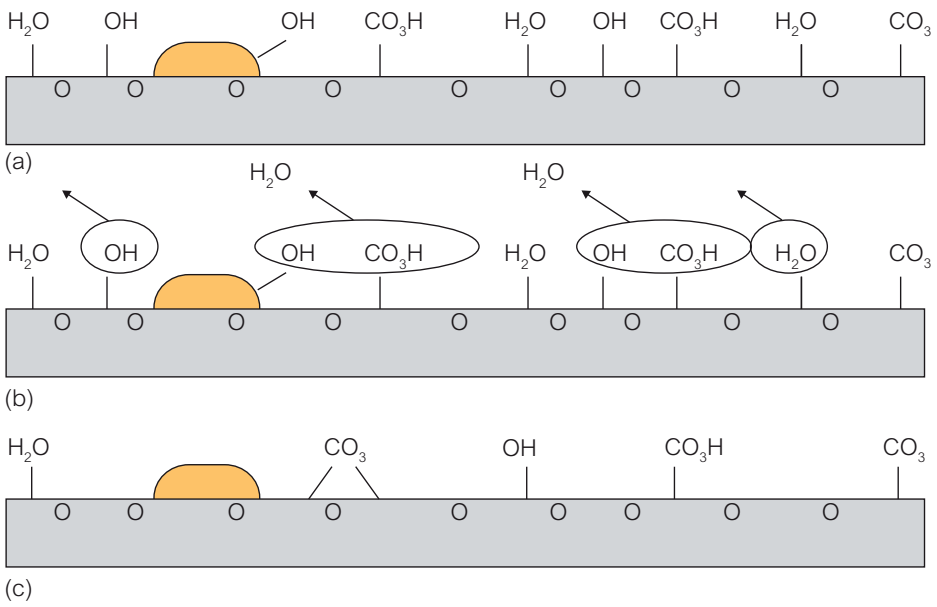


Scheme 2



Some of these OH groups decompose with the available bicarbonates to form the stable carbonate species on the catalyst surface as depicted by reaction scheme 2.

Figure 2

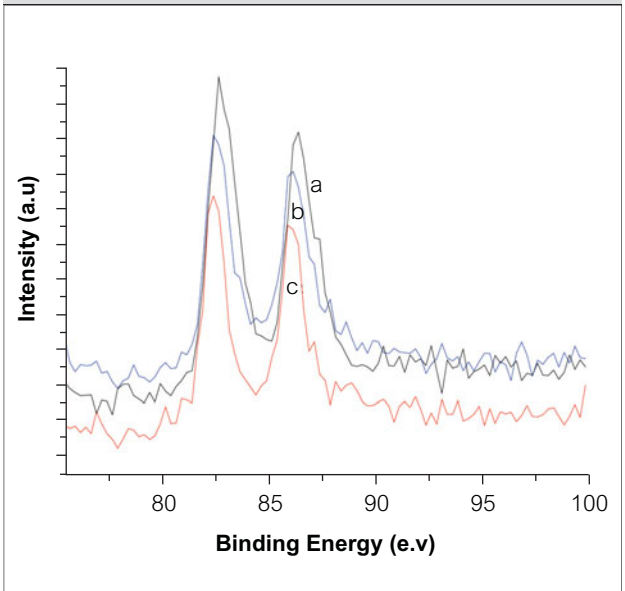


Depiction of a catalyst surface(a) after preparation; (b) during storage; and (c) just before reaction as visualized, guided by Infrared data

Infrared spectra show that the water molecules formed during reaction 2 does not re-adsorb on the catalysts surface to hydrolyse the carbonate species. The amount of OH groups present on the surface of the catalyst during storage is dependent on the storage environment and greatly affects the activity of the catalyst. The phenomenon shown in Figure 2 also occurs during storage, but takes place faster under vacuum.

XPS results indicate that storage of the catalysts under vacuum results in a decreased amount of gold nanoparticles detected on the surface of the catalyst. This is shown by the lower intensity of both the Au4f peaks compared to those of the catalysts stored in air and in nitrogen (Figure 3). This can be interpreted as agglomeration or entrapment of nanoparticles in the support matrix. Agglomeration of Au nanoparticles is accompanied by a decrease in the binding energy of the Au atoms on all stored catalysts but a larger shift in binding energy was observed for the catalyst stored in vacuum where the binding energy decreased from 83.7 eV to 83.2 eV. The decrease in binding energy is an indication that Au nanoparticles on this catalyst contain more reduced Au atoms. XPS clearly shows changes on the binding energies of the catalysts after storage. Although some of these changes may be due to XPS irradiation [9, 11], it is anticipated that most of it is due to the changes that occur during storage.

Figure 3



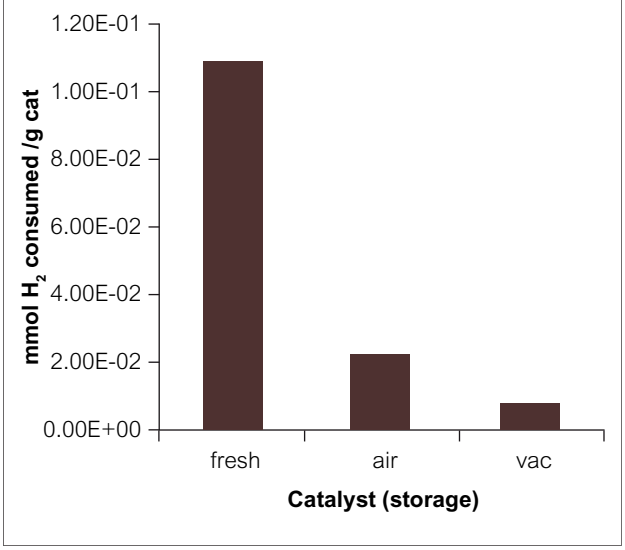
XPS spectra of catalysts stored in the light under various environments; (a) Nitrogen; (b) Air; (c) Vacuum

Table 2

Storage environment	TEM	Au	% atom (surface)			
	nm	B.E.	C	O	Ti	Au
Fresh	**3.1**	**83.7**	**11.1**	**61.8**	**25.9**	**0.8**
Vacuum	6.8	83.2	25.2	53.2	21.3	0.2
Air	6.3	83.2	21.3	55.8	22.6	0.3
Nitrogen	5.3	83.5	27.1	51.3	21.2	0.4

Summary of XPS and TEM results for catalysts stored in the light

Figure 4

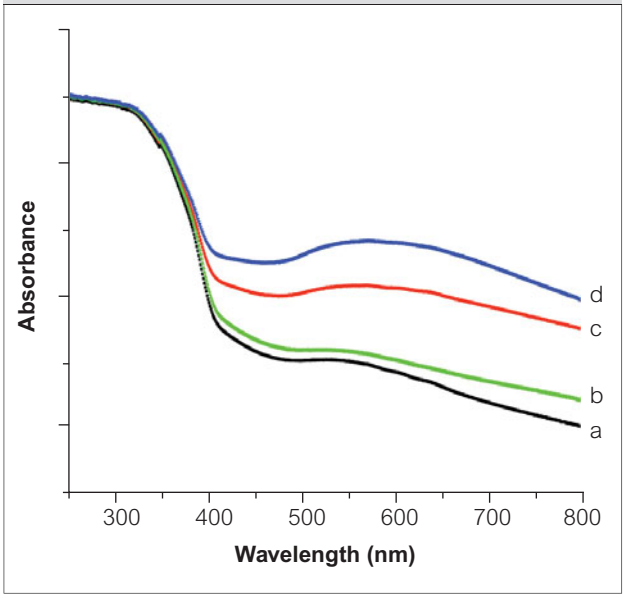


Catalysts stored under various environments: (a) Fresh; (b) Air; (c) Vacuum

P-TPR indicates significantly more Au(III) in the fresh catalyst compared to catalysts stored under air and vacuum. This is shown by the smaller amount of hydrogen consumed by the catalysts after storage under various environments compared to that consumed by the fresh catalyst (Figure 4). TEM results (Table 2) show an agglomeration of Au nanoparticles, which is most likely accompanied by the reduction of Au(III).

Oxidation state of catalysts stored in the light under various environments (nitrogen, air and vacuum) was investigated by UV-vis spectroscopy. A UV-vis band around 600 nm, which is a surface plasmon resonance band of reduced Au nanoparticles, is observed in Figure 5. This band is stronger for the

Figure 5



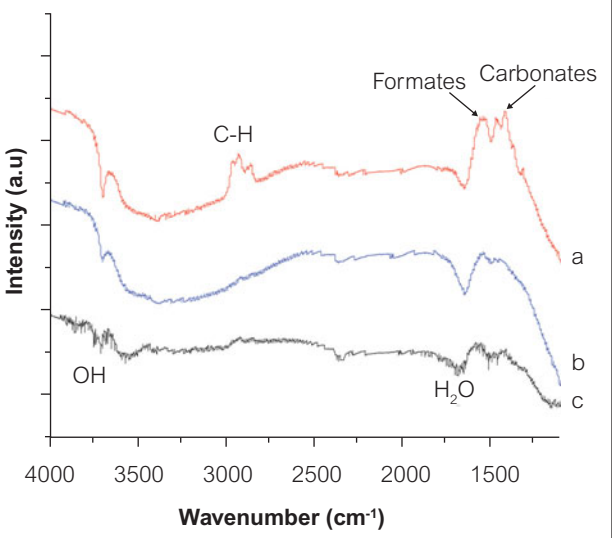
UV-vis spectra of catalysts stored under different environments: (a) Fresh; (b) Nitrogen; (c) Air; (d) Vacuum

catalyst stored in vacuum than for those stored in other environments. This is an indication that storage under vacuum increases the reduction of Au nanoparticles. The reduction of Au(III) to Au0 nanoparticles is accompanied by agglomeration, as was observed from the TEM results in Table 2, which shows that particle size of the catalyst stored in the light increased from 3.1 to 6.8 nm. The combination of vacuum and light seems to exacerbate the degree of reduction and agglomeration of Au nanoparticles compared to storage in the light under nitrogen. Yang *et al*. [13] also observed a consistent increase in the particle size of Au with increasing reduction of ionic Au.

3.1.2 Storage in the dark (ambient temperature)

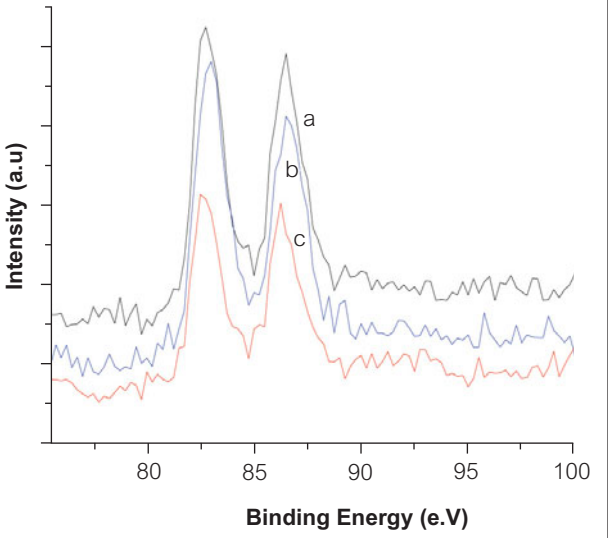
Infrared spectra of the catalysts stored in the dark shows similar behaviour to those stored in the light at ambient temperature. However, a decreased amount of formate and carbonate species is observed on the catalysts stored under air in the dark (Figure 6) compared to those stored under air in the light (Figure 1). The catalyst stored in the dark under nitrogen (Figure 6c) shows smaller negative peaks at 1620 cm^{-1}, 3700 cm^{-1} and between 4000-3000 cm^{-1} corresponding to the loss of moisture and hydroxyl groups as also found in Figure 1c. This loss of moisture on the catalyst stored in nitrogen is not accompanied by the formation of formate and carbonate species on the surface of the catalyst.

Figure 6



Infrared spectra of Au/TiO_2 catalyst stored in the dark under various environments: (a) Vacuum; (b) Air; (c) Nitrogen

Figure 7



XPS spectra of catalysts stored in the dark under various environments: (a) Nitrogen; (b) Air; (c) Vacuum

However, Figure 6b and 6c show that storage of the catalyst at atmospheric pressure reduces the amount of surface species accumulation.

XPS results of the samples stored in the dark reveal that storage of the catalysts under vacuum results in a decreased amount of gold nanoparticles detected on the catalyst surface (Figure 7). This is shown by the lower intensity of both the Au4f peaks compared to those of the catalysts stored under air and nitrogen in the dark. The same behaviour was observed for the catalysts stored in the light.

TEM results (Table 3) also indicate an increase in gold particle size during storage in the dark compared to fresh catalysts.

3.1.3 Storage in the dark (~4°C)

Compared to the catalysts stored in light and in dark environments at ambient temperature, refrigeration of the catalyst reduces the formation and accumulation of surface species on the surface of the catalyst. However, a considerable amount of moisture seems to have been lost and traces of formates were formed on the catalysts stored under vacuum as evidenced by C-H stretches depicted by the bands at 2950 and 2850 cm^{-1} (Figure 8); the amount is less than that observed in Figures 1 and 6. No formate and carbonate species were formed on the catalysts stored under air and nitrogen.

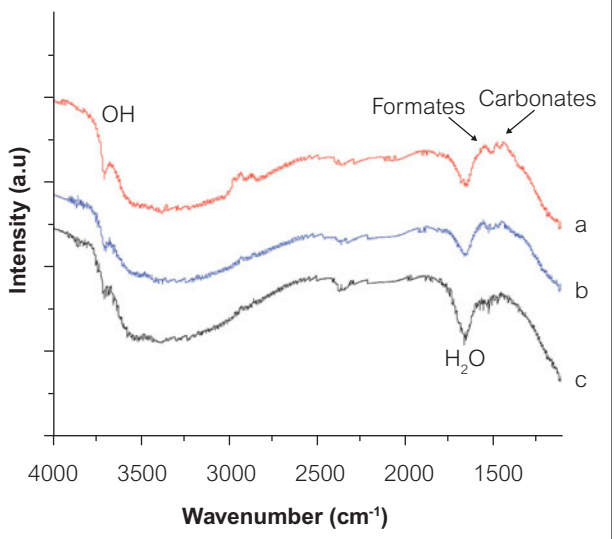
Table 3

Storage environment	TEM	Au	% atom (surface)			
	nm	B.E.	C	O	Ti	Au
Fresh	**3.1**	**83.7**	**11.1**	**61.8**	**25.9**	**0.8**
Vacuum	7.8	83.2	37.1	45.7	17.0	0.2
Air	n.d.	83.5	29	50.3	20.0	0.3
Nitrogen	n.d.	83.3	35.7	46.7	17.3	0.3

Summary of XPS and TEM results for catalysts stored in the dark

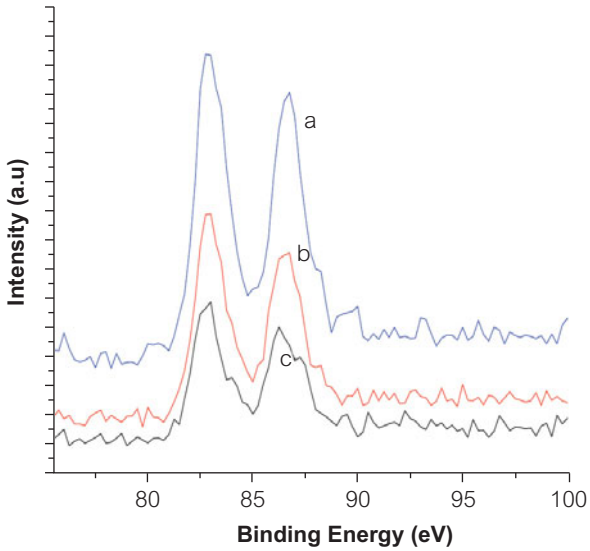
Evidence of particle size agglomeration is shown by the decrease in the size of the XPS peaks of the catalysts stored under vacuum (Figure 9c), compared to that stored under nitrogen. The difference in sizes of the peaks in Figure 9 is greater than for those in Figures 3 and 7. In contrast to storage at ambient temperature, agglomeration of gold nanoparticles appears to be less as indicated by the TEM results (Table 4) and is not accompanied by a big shift from higher to lower binding energy. Storage under vacuum results in smaller Au4f peaks compared to those of the catalysts stored under nitrogen, due to agglomeration of nanoparticles.

Figure 8



Infrared spectra of Au/TiO_2 catalyst stored in the dark at ~4°C (refrigerator) under various environments: (a) Vacuum; (b) Air; (c) Nitrogen

Figure 9



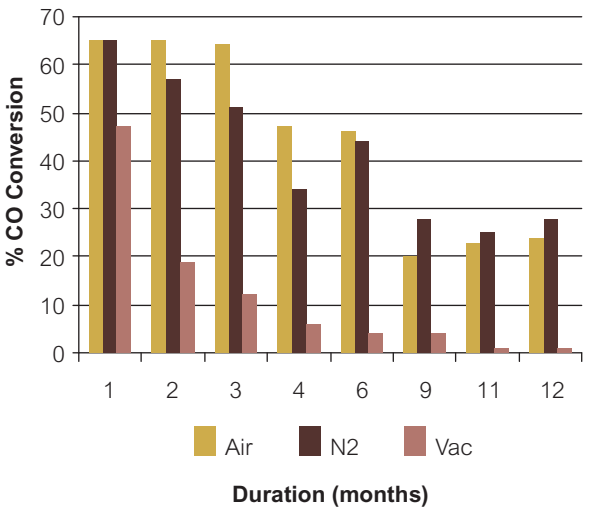
XPS spectra of catalysts stored in the dark (~4°C) under various environments: (a) Nitrogen; (b) Air; (c) Vacuum

Table 4

Storage environment	TEM	Au	% atom (surface)			
	nm	B.E.	C	O	Ti	Au
Fresh	**3.1**	**83.7**	**11.1**	**61.8**	**25.9**	**0.8**
Vacuum	5.7	83.5	38.0	49.3	12.5	0.2
Air	5.4	83.5	37.8	45.1	16.8	0.3
Nitrogen	2.9	83.5	25.1	52.7	21.7	0.5

Summary of XPS and TEM results for catalysts stored in the dark (~4°C)

Figure 10



Effect of storage in the light on the activity of Au/TiO_2 catalyst

3.2 CO Oxidation

3.2.1 Catalytic activity of the catalysts stored in the light

Figure 10 shows a decrease in the activity of the catalyst stored under air and nitrogen after twelve months. By this time, most of the catalyst granules had already changed colour to purple. However, the catalyst was thoroughly mixed before analysis. The activity of the catalyst stored under vacuum decreases much quicker than the activities of those stored under nitrogen and air. This is consistent with increased Au nanoparticles size and carbonate formation on the surface of the catalyst as shown in Figure 1 and Table 2. The XPS data in Table 2 shows that the amount of Au on the surface of the catalyst stored under vacuum decreases from 0.8% to 0.2% after 12 months. The decrease in the amount of Au on the surface of the catalysts results in the decrease in the amount of the active sites required for high catalytic activity.

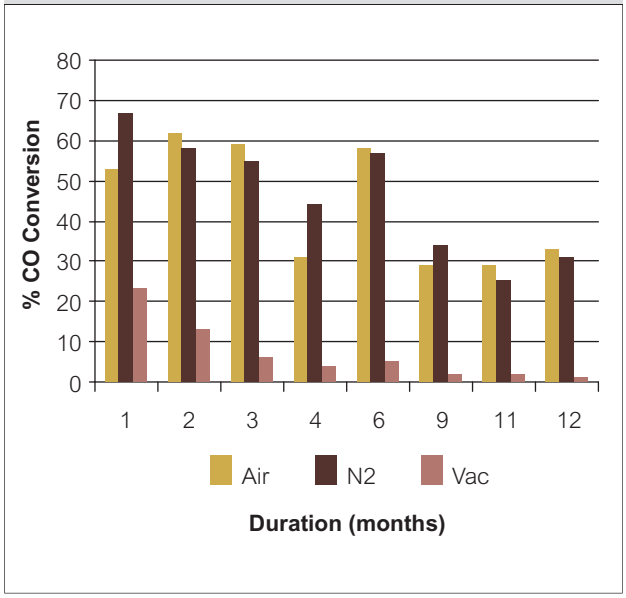
3.2.2 Catalytic activity of the catalysts stored in the dark

Over the period of 12 months, it is evident from Figure 11 that storing the catalyst under air and nitrogen in the dark atmosphere preserves the activity much better than storage under vacuum. The catalyst stored under vacuum quickly changes its colour from whitish-grey to purple, while no colour change was observed over the first few months for catalysts stored under air and nitrogen. However, over time, those catalysts stored under air and nitrogen do gradually change colour to purple, but not as dark as those stored under vacuum. Colour change to purple has been associated with particle size increase and reduction of oxidic Au to metallic Au. Tables 2, 3 and 4 shows that the catalysts stored under vacuum undergo an increase in size of the Au nanoparticles. The decrease in activity of these catalysts, particularly those stored under vacuum, is also caused by the removal of moisture and hydroxyl groups from the surface, as confirmed the IR data in Figure 6. The presence of hydroxyl groups on the Au catalyst has been reported to be vital for high activity [5]. The decrease in the activity of this catalyst is also caused by the increase in the particle size of Au as shown by the TEM results in Table 3.

3.2.3 Catalytic activity of the catalysts stored in the dark (~4°C)

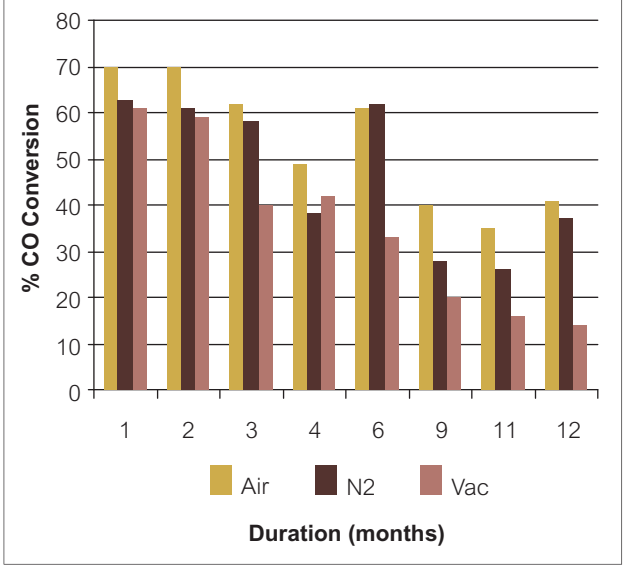
Figure 12 shows that storage in the refrigerator preserves the catalyst much better than storage in the dark and the light, even under vacuum. Up to 12 months the catalyst stored in the refrigerator has not completely changed colour to purple as compared to those stored in the dark and the light. It shows that even though some moisture was removed by the vacuum storage process, a considerable amount of hydroxyl groups are still present on the surface of the catalyst, which provides good activity to convert CO into CO_2 compared to those catalysts stored at room temperature under vacuum that had lower activity. The lower activity of the catalyst stored under vacuum in the refrigerator compared to those stored under air and nitrogen in the refrigerator is due to the loss of moisture and hydroxyl groups confirmed by infrared data in Figure 8a. The lower activity is also consistent with the decrease in the amount of surface Au and agglomeration as shown by XPS data in Figure 9 and Table 4. The higher activity of the catalyst stored in the refrigerator under vacuum compared to those stored under vacuum in the light and the dark environments is seemingly due to the absence of formate and carbonate species on the surface.

Figure 11



Effect of storage in the dark on the activity of Au/TiO_2 catalyst

Figure 12



Effect of storage in the dark (~4°C) on the activity of Au/TiO_2 catalyst

Conclusions

Gold catalysts for CO oxidation deactivate during storage. The data presented in this paper reveals that there are various factors contributing to the deactivation of gold catalysts. These include

reduction of ionic Au, agglomeration of Au nanoparticles, loss of hydroxyl groups and moisture as well as formation and accumulation of carbonate and formate species on the surface. Storing the catalyst in the refrigerator reduces the extent of Au reduction and Au particle agglomeration as well as the formation of carbonate species compared to catalysts stored at room temperature in the light or the dark. Storage under vacuum significantly accelerates catalyst deactivation through Au reduction and particle agglomeration, loss of surface hydroxyls and moisture, and accumulation of carbonates and formates.

It is therefore recommended that catalysts be thoroughly purged with inert gas to remove all the atmospheric and adsorbed CO_2 from the catalyst and the catalysts should be stored in a refrigerator or at least a cool and dark place to minimise the effects of temperature and light.

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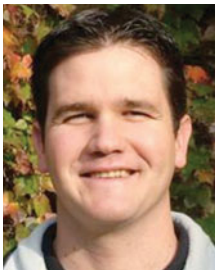

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